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## Spin Glass Behavior in URh<sub>2</sub>Ge<sub>2</sub>

S. Süllow, G. J. Nieuwenhuys, A. A. Menovsky,\* and J. A. Mydosh

*Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9506, 2300 RA Leiden, The Netherlands*

S. A. M. Mentink<sup>†</sup> and T. E. Mason

*Department of Physics, University of Toronto, 60 Saint George Street, Toronto, Ontario, Canada M5S 1A7*

W. J. L. Buyers

*AECL Research, Chalk River, Ontario, Canada K0J 1J0*

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URh<sub>2</sub>Ge<sub>2</sub> occupies an extraordinary position among the heavy-electron 122 compounds, by exhibiting a previously unidentified form of magnetic correlations at low temperatures instead of the usual antiferromagnetism. Here we present new results of ac and dc susceptibilities, specific heat, and neutron diffraction on single-crystalline as-grown URh<sub>2</sub>Ge<sub>2</sub>. These data clearly indicate that crystallographic disorder on a local scale produces spin glass behavior in the sample. We therefore conclude that URh<sub>2</sub>Ge<sub>2</sub> is a 3D Ising-like, random-bond, heavy-fermion spin glass. [S0031-9007(96)02019-4]

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URh<sub>2</sub>Ge<sub>2</sub> is a heavy-fermion intermetallic compound ( $\gamma \approx 130$  mJ/molK<sup>2</sup>) for which there has been a long-standing controversy concerning the magnetic ground-state. Usually in the 122 compounds with uranium a simple antiferromagnetic (AF) stacking occurs along the *c* axis of U moments, ferromagnetically coupled in the *a-b* planes and directed parallel to *c* (AF-I structure). In these materials, if the Kondo effect does not dominate, a distinct phase transition takes place to the long-range ordered magnetic ground state. In particular, there has recently been a great deal of systematic study and classification of the various U 122 systems [1] and a standard description (the Doniach model [2]) has emerged which involves the competition between the RKKY interaction, leading to magnetic order, and the Kondo effect which compensates the moments, thereby eliminating the phase transition.

However, URh<sub>2</sub>Ge<sub>2</sub> does not belong to this well-understood category. Early neutron scattering experiments [3] on polycrystalline samples did not find magnetic ordering and could not unambiguously determine a unique crystal structure. Two solutions were proposed: (i) a structure related to body-centered tetragonal (bct) ThCr<sub>2</sub>Su<sub>2</sub> (*I4/mmm*), but with lower symmetry (*P4/mmm*) due to randomly distributed Rh and Ge on the Cr and Si sites, and, (ii) an atomically ordered CaBe<sub>2</sub>Ge<sub>2</sub> (*P4/nmm*) unit cell. We repeated the powder neutron diffraction experiments and reached similar conclusions [4]. However, a peak in the static susceptibility  $\chi_{dc}$  indicated an “antiferromagnetic” transition takes place at 8 K [3]. Other investigations [5] claimed that a drop in the resistivity indicated magnetic order below 2 K. Later, Lloret *et al.* [6] showed that the varying behavior of URh<sub>2</sub>Ge<sub>2</sub> is governed by the stoichiometry, which shifts both the  $\chi_{dc}$  maximum and the resistivity drop. The confusion was complete when the first data on single-crystalline

URh<sub>2</sub>Ge<sub>2</sub> appeared [7]. Now it was concluded that no long-range magnetic order occurs down to 35 mK, but the maximum detected in  $\chi_{dc}$  at 11 K and the change in slope of the specific heat at 12 K were tentatively interpreted as arising from crystalline electric field effects.

In these previous investigations an intriguing possibility was overlooked, namely, that spin-glass freezing occurs. But how can a spin-glass state be possible without some kind of randomness or disorder? Intermetallic compounds are customarily thought of as possessing a relatively perfect periodic crystal structure. Motivated by the recent resurgence of interest in spin glasses, especially their formation with *f* elements and their novel quantum properties [8,9], we have reopened the unsolved case of URh<sub>2</sub>Ge<sub>2</sub> by investigating a new single crystal. Our bulk measurements of the ac susceptibility  $\chi_{ac}$ , static susceptibility  $\chi_{dc}$ , specific heat  $c_p$ , and elastic neutron scattering clearly show this system to be an archetypal spin glass. We propose that the disorder derives from an amalgamation of the ThCr<sub>2</sub>Si<sub>2</sub> and the CaBe<sub>2</sub>Ge<sub>2</sub> structures and causes an intermixture of Rh and Ge positions. This in turn creates random bonds which lead to competing magnetic interactions.

A crystal of URh<sub>2</sub>Ge<sub>2</sub> was grown using the Czochralski technique in a tri-arc furnace. X-ray Laue diffraction proved the sample to be truly single-crystal, and electron probe microanalysis showed it to be single phase with proper stoichiometry URh<sub>2.00±0.06</sub>Ge<sub>1.96±0.06</sub>. Here we report solely on the as-grown crystal. The effect of various heat treatments on the magnetism will be reported elsewhere [4,10]. Measurements of  $\chi_{ac}$  and  $\chi_{dc}$  were performed with a Quantum Design SQUID between  $T = 1.8$  and 300 K in magnetic fields up to 5 T;  $c_p$  was determined using a semiadiabatic heat-pulse method from 1.8 to 30 K in fields up to 6 T. Elastic neutron

scattering measurements at low  $T$  were performed at the triple-axis spectrometer C5 at AECL using a Ge (111) monochromator, a sapphire and pyrolytic graphite (PG) filter to reduce higher order contamination in the beam, and the (002) reflection from PG as an analyzer. The energy resolution as measured with vanadium was  $\Delta E = 0.162$  THz, half-width at half maximum. The results of recent  $\mu^+$ SR experiments will be reported elsewhere [11].

Figure 1 shows the real and imaginary parts of  $\chi_{ac}$  versus  $T$  at different frequencies  $\omega$  for the 3.5 G driving field  $B\|a$  and  $B\|c$ . Note the sharp cusps in  $\text{Re}(\chi_{ac})$  at 9.6 K denoting the freezing temperatures  $T_f$  and how  $T_f$  shifts to higher temperatures with increase of  $\omega$ .  $\text{Im}(\chi_{ac})$  appears at a much smaller step whose point of inflection also designates  $T_f$  [ $\chi''_{ac} \approx -(\pi/2)\partial\chi'_{ac}/\partial(\log_{10}\omega)$ ] and its frequency dependence. By way of the above criteria for  $\chi'_{ac}$  and  $\chi''_{ac}$  we can calculate the initial frequency shift of  $T_f$ :

$$\delta T_f = \frac{\Delta T_f}{T_f \Delta \log_{10} \omega} = 0.025 \pm 0.005 \quad (1)$$

for both crystallographic directions. This value is typical for metallic spin glasses, e.g.,  $\text{CuMn}:0.005$  and  $(\text{La,Gd})(\text{La,Gd})\text{Al}_2:0.06$ . In addition to this canonical spin glass behavior [12] the low- $T$  ( $T \ll T_f$ ) forms of  $\chi_{ac}$  are standard regarding both  $\omega$  and  $T$  dependences. The susceptibilities measured along the  $c$  axis are much larger than those in the basal plane, indicating that the preferred spin orientation is randomly up/down parallel to

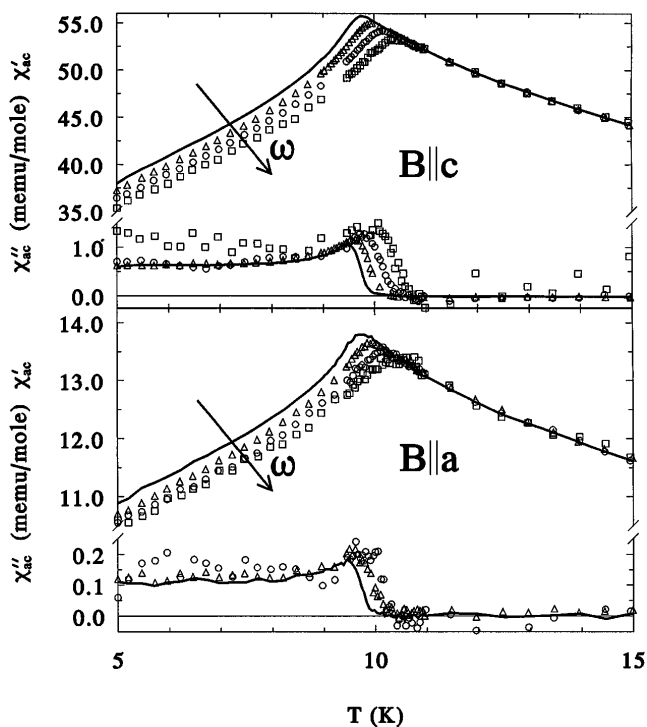


FIG. 1. The frequency dependence of the ac susceptibility (in-phase  $\chi'_{ac}$  and out-of-phase  $\chi''_{ac}$ ) of  $\text{URh}_2\text{Ge}_2$  for the two crystallographic directions. (—): 1.157 Hz, ( $\Delta$ ): 11.57 Hz, ( $\circ$ ): 115.7 Hz, ( $\square$ ): 1157 Hz.

$c$ . Thus there is an Ising-like character to the spin glass freezing.

Figure 2 displays the zero-field-cooled (ZFC) and field-cooled (FC) magnetization ( $\chi_{dc} = M/B$  with  $B = 50$  G) for both  $a$  and  $c$  axes. Here a small maximum appears at 9.3 K with irreversibility starting just below this temperature. Such behavior reveals the static freezing temperature  $T_f(\omega \rightarrow 0)$  to be less than  $T_f$  at higher frequencies. The maximum in  $\chi_{dc}$  is smeared out by the application of a static magnetic field  $B_{dc}$ . For  $T < 9$  K the FC- $\chi_{dc}$  is essentially constant and independent of measurement time as expected, while ZFC- $\chi_{dc}$  continues to decrease and is time dependent. If on this FC branch we set the field to zero at a constant  $T$ , we generate an isothermal remanence magnetization (IRM) which relaxes over many decades of time (not shown) according to the roughly logarithmic time dependence expected for a spin glass [12].

In Fig. 3 we show the magnetic specific heat of  $\text{URh}_2\text{Ge}_2$  plotted as  $c_p$  vs  $T$  and  $c_p/T$  vs  $T$ . We have corrected for the lattice contribution to  $c_p$  by subtracting the specific heat of  $\text{UF}_2\text{Ge}_2$  which represents a Pauli paramagnetic reference compound. Neither U nor Fe is magnetic and a simple mass scaling was used to correct for the different masses of Fe and Rh [13]. From Fig. 3 it can be seen that  $c_p$  is featureless below 10 K, while a broad maximum appears in  $c_p/T$  above 10 K, which becomes smeared in an applied magnetic field. At low  $T$ ,  $c_p$  varies between  $T$  and  $T^2$  and is independent of field. To determine  $\gamma$  we plot  $c_p/T = \gamma + DT^\kappa$ , with  $D$  and  $\kappa$  as free parameters and  $\gamma$  the intercept. An effective  $\gamma \approx 130$  mJ/mole  $\text{K}^2$  is estimated in the limit  $T \rightarrow 0$ , while  $D = 19$  mJ/mole  $\text{K}^{\kappa+2}$  and  $\kappa = 0.91$  [4]. The above properties are typical for a canonical spin glass with the overall curves in Fig. 3 closely resembling those of  $\text{CuMn}$  [12].

To further investigate the structural and magnetic properties of as-grown single crystals, we performed elastic

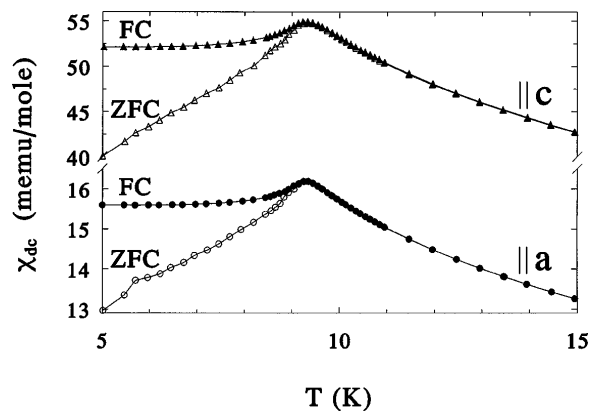


FIG. 2. dc susceptibility  $\chi_{dc}$  of as-grown single crystal  $\text{URh}_2\text{Ge}_2$  in a field-cooled (filled symbols) and zero-field-cooled (open symbols) experiment in an applied field  $B = 50$  G.

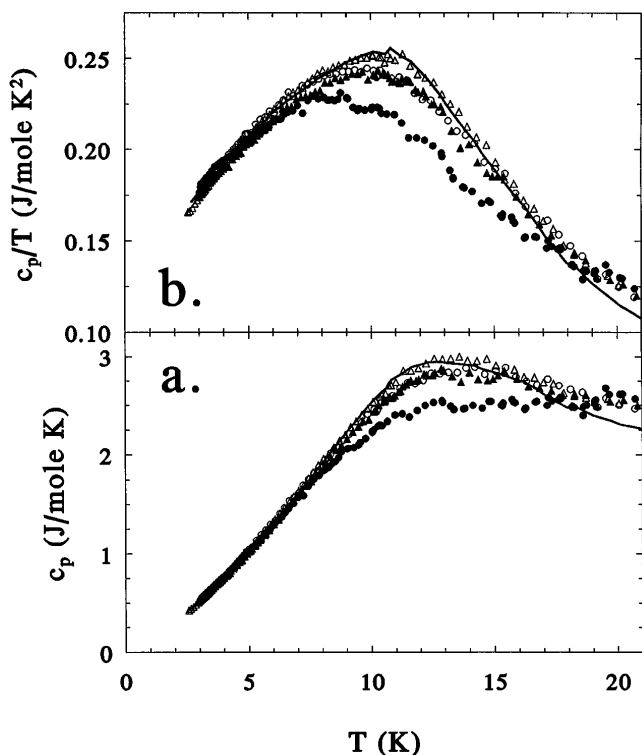


FIG. 3. (a)  $c_p$  vs  $T$  of as-grown  $\text{URh}_2\text{Ge}_2$ , corrected for the lattice contribution, in fields of 0 T (—), 3 T ( $\Delta$ ), 6 T ( $\circ$ ) for  $B||a$  and 3 T (filled  $\Delta$ ), 6 T ( $\bullet$ ) for  $B||c$ . (b) The specific heat from (a), plotted as  $c_p/T$  vs  $T$ .

neutron scattering measurements, with the crystal oriented in the  $(h0l)$  zone. The lattice parameters at 4.3 K are  $a = 4.160 \text{ \AA}$  and  $c = 9.733 \text{ \AA}$ , in good agreement with Ref. [7], and correspond to the correct 122 stoichiometry as found by Lloret *et al.* [6]. The structural intensities, integrated in both  $a^*$  and  $c^*$  directions, have been reported before [14] and are close to the values calculated for the two suggested structures discussed above. However, anomalously high intensities of the  $(0l)$  reflections ( $l = 2-7$ ) have been observed. These can only partly be explained by possible extinction or multiple scattering effects, since the crystal is small ( $10 \times 3 \times 3 \text{ mm}^3$ ) and the difference between measured and calculated intensities of the  $(0l)$  reflections is an irregular function of  $l$ . Moreover, decreases in these intensities occur after annealing the crystal [10], and this indicates better structural order. The small difference in neutron scattering lengths of Rh and Ge does not allow for a straightforward explanation of large intensity differences. We must invoke a more complicated mixture of Rh and Ge atoms, together with a distribution of the free positional  $z$  parameters of Rh and Ge, and the presence of a small amount ( $<5\%$ ) of vacancies to account for the increased intensities. Also, the observed weak structural  $(100)$  reflection, forbidden in both  $P4/mmm$  and  $P4/nmm$  symmetries, points to a disordered crystal structure. Certainly the large value of

the resistivity at 300 K (as high as  $500 \mu\Omega \text{ cm}$ ) implies a substantial amount of randomness [4,7]. Both powder x-ray data [6,7] and our single-crystal neutron results indicate that the U atoms occupy their regular sites, forming a bct sublattice. Thus the disorder is only on the nonmagnetic ligand sites, leading to the conclusion that  $\text{URh}_2\text{Ge}_2$  should be regarded as a three-dimensional “random bond” spin glass.

In Fig. 4 we present the elastic neutron intensity versus  $T$  at the  $(100)$  position. Superimposed on the small nuclear intensity, weak magnetic scattering is observed that is *not* resolution limited. Much weaker magnetic scattering has also been found at  $(102)$ , consistent with an easy  $c$  axis as derived from the susceptibility data. The lower inset in Fig. 4 shows a scan along  $(h00)$  at 4.3 K, corrected for background using similar data at 20 K, where the solid line is the momentum resolution measured by removing the PG filter from the incident beam to allow  $\lambda/2$  scattering of the strong  $(200)$  nuclear reflection. An onset of elastic magnetic scattering occurs at  $T_f = 16.2 \pm 0.4 \text{ K}$ . This signals development of magnetic correlations on the time scale set by the energy resolution  $\tau > h/\Delta E = 6.0 \times 10^{-12} \text{ s}$ . We cannot reliably estimate the size of the fluctuating U moment, since this would require integration over all energies and wave vectors.  $\mu^+$ SR measurements show the onset below 13 K of correlations, which are static on a time scale of  $10^{-8} \text{ s}$  [11]. In the  $\chi_{dc}$  and low-frequency ( $\omega < 1157 \text{ Hz}$ )  $\chi_{ac}$

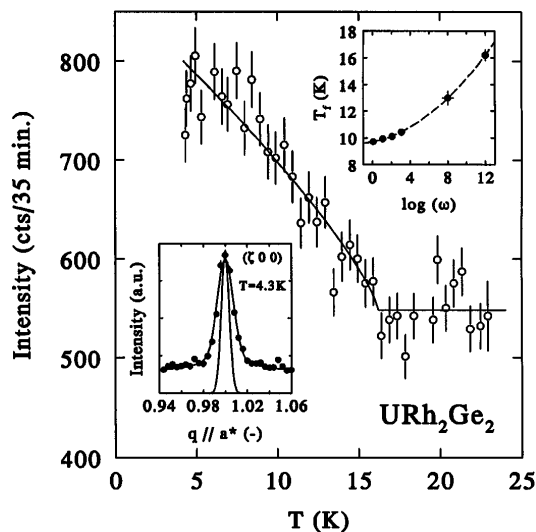


FIG. 4. Elastic neutron scattering at  $Q = (100)$  versus temperature, showing the onset of magnetic correlations slower than  $10^{-12} \text{ s}$  below  $T_f = 16.2 \text{ K}$ . The line is a guide to the eye. The lower inset shows a  $Q$  scan along  $(a^*00)$  at 4.3 K, corrected for background provided by similar data at 20 K, with the solid line a fit to Eq. (2), giving the magnetic correlation length. The  $Q$  resolution is also indicated. The frequency dependence of  $T_f$ , derived from  $ac$  susceptibility,  $\mu^+$ SR, and neutron scattering is shown in the upper inset, over 12 decades of frequency. The line is a guide to the eye.

experiments correlations that are static on a time scale of  $10^{-3}$  s develop only below 10 K. One of the defining characteristics of a spin glass is its frequency dependence of  $T_f$  [12]. The upper inset in Fig. 4 collects these data and shows the significant increase of  $T_f$  versus  $\log(\omega)$  over 12 orders in frequency, firmly establishing the spin-glass nature of URh<sub>2</sub>Ge<sub>2</sub>. By employing a model assuming exponentially fast decaying spin-spin correlations,  $\langle S_R^c S_{R+r_c}^c \rangle \propto \exp(-\kappa_c r_c)$  (with  $\kappa_c$  the inverse correlation length along the  $c$  direction), previously used for URu<sub>2</sub>Si<sub>2</sub> [15], we can estimate the magnetic correlation lengths in the  $a$  (using the same formalism) and  $c$  directions. The Fourier-transformed correlation function becomes

$$\langle S_q^c S_{-q}^c \rangle = \langle S^c \rangle^2 \frac{\sinh(\kappa_c c)}{\cosh(\kappa_c c) - \cos(q_c c)}. \quad (2)$$

The solid line through the  $Q$  scan in the lower inset of Fig. 4 is a fit to Eq. (2). This procedure yields magnetic correlation lengths of  $\xi_a^m = 45 \pm 5 \text{ \AA}$  and  $\xi_c^m = 74 \pm 10 \text{ \AA}$ , much shorter than for better-ordered URu<sub>2</sub>Si<sub>2</sub> [15].

The sensitivity of the crystal structure of URh<sub>2</sub>Ge<sub>2</sub> to the Rh/Ge stoichiometry resembles the now well-understood case of isoelectronic UCo<sub>2</sub>Ge<sub>2</sub>, where the  $I4/mmm$  and  $P4/mmm$  structures are formed, depending on the exact stoichiometry [1]. In the  $I4/mmm$  structure, UCo<sub>2</sub>Ge<sub>2</sub> orders as a long-range AF with  $T_N = 175$  K. In the  $P4/mmm$  structure, with much smaller unit-cell volume, no magnetic order is found down to 0.3 K. The case of URh<sub>2</sub>Ge<sub>2</sub>, with a  $c$ -axis length in between the two extremes of UCo<sub>2</sub>Ge<sub>2</sub>, thus appears to be even more subtle than UCo<sub>2</sub>Ge<sub>2</sub>.

The experimental properties of URh<sub>2</sub>Ge<sub>2</sub> resemble the “non-Fermi-liquid-like” transport and thermodynamic properties of the *intentionally* diluted system UCu<sub>5-x</sub>Pd<sub>x</sub> [16,17]. A moderately disordered Kondo model, recently proposed by Miranda *et al.* [18] successfully explains the distribution of internal fields as measured by NMR [16]. Without adjustable parameters, it can describe the susceptibility, specific heat, and scaling behavior in  $\omega/T$  observed by neutron scattering [17]. Recently, indications of possible spin-glass freezing in UCu<sub>5-x</sub>Pd<sub>x</sub> ( $x = 1$ ) were found in magnetization experiments, with  $T_f \simeq 100$  mK [19].

In conclusion, all the measured bulk properties of the uranium compound URh<sub>2</sub>Ge<sub>2</sub> are those of an archetypal spin glass. Neutron scattering showed that short-range magnetic correlations develop on time scales of  $10^{-12}$  s, in a highly disordered lattice.  $T_f$  increases with frequency over twelve decades, providing unambiguous proof for spin-glass behavior. To further explore the exact nature of the structural disorder in this compound, local experimental probes such as EXAFS and NMR are needed. This would allow direct comparison with the disordered Kondo model. Finally, a novel quantum critical point

[9] is expected for the metallic quantum paramagnet to metallic spin-glass transition as the freezing temperature is driven towards zero with, e.g., pressure or increased disorder. Such high-pressure experiments seem favorable in URh<sub>2</sub>Ge<sub>2</sub> and are presently planned.

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\*Also at Van der Waals-Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands.

†Present address: Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands.

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